

Supporting Information

Transition from Lamellar to nanostructure mesophases in azobenzene-based hockey-stick polycatenars

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1. Synthesis and Analytical Data

1.1 Characterization methods

Thin layer chromatography (TLC) was performed on aluminium sheet precoated with silica gel. Analytical quality chemicals were obtained from commercial sources and used as obtained. The solvents were dried using the standard methods when required. The purity and the chemical structures of all compounds synthesized were confirmed by the spectral data. The structure characterization of the synthesized polycatenars is based on ¹H-NMR and ¹³C-NMR. Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

1. 2. Synthesis of the new hockey-stick polycatenars

The final HS polycatenars are synthesized as shown in Scheme 2. The benzoic acid derivatives **1/n** were synthesized as reported recently,[S1] while the protected bent-core unit 4-benzyloxy-2-hydroxybenzotrile is synthesized using the method reported in Ref. [S2]. The synthesis details of the remaining intermediates and the final HS molecules **B6/n** and **B10/n** along with their analytical data are given below.

2/n. The benzoic acid derivative **1/n** (1 eq.) was converted to the corresponding acid chloride by refluxing in excess thionylchloride (SOCl₂) under argon atmosphere for one hour. The excess thionylchloride was removed under vacuum and the obtained acid chloride was dissolved in anhydrous dichloromethane (DCM) followed by addition of 4-benzyloxy-2-hydroxybenzotrile (1 eq.), triethylamine (1.2 eq.) and few drops of dry pyridine and stirred under reflux for 6 hrs. The reaction progress was checked with TLC and at the end the reaction mixture was cooled down to room temperature, poured into 10 mL of an aqueous solution of 1 N HCl. The organic layer was separated and washed twice with saturated aqueous NaHCO₃ solution. The combined aqueous washes were extracted with DCM, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The crude orange materials were purified by column chromatography using DCM followed by recrystallization from DCM:ethanol mixture (1:1) to yield the desired final compounds.

2/6. Yield 77.35%, white solid, m.p. ~ 126-128 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 4H, Ar-H), 7.70 – 7.58 (m, 5H, Ar-H), 7.45 – 7.25 (m, 11H, Ar-H), 7.11 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.96 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 5.13 (s, 2H, -OCH₂ph), 4.17 – 3.93 (m, 6H, -OCH₂CH₂), 1.93 – 1.67 (m, 6H, -OCH₂CH₂CH₂-), 1.61 – 1.26 (m, 18H, CH₂), 1.01 – 0.79 (m, 9H, CH₃).

2/10. Yield 67.69%, white solid, m.p. ~ 49-51 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 4H, Ar-H), 7.72 – 7.60 (m, 5H, Ar-H), 7.48 – 7.27 (m, 11H, Ar-H), 7.14 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.98 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 5.15 (s, 2H, -OCH₂ph), 4.14 – 3.98 (m, 6H, -OCH₂CH₂), 1.94 – 1.68 (m, 6H-OCH₂CH₂CH₂-), 1.67 – 1.10 (m, 42H, CH₂), 1.03 – 0.76 (m, 9H, CH₃).

3/n. Compound **2/n** (3.48 mmol) was dissolved in 80 ml of dry THF followed by addition of Pd/C (10% Pd, 0.3 g) and flushed with hydrogen. The mixture was stirred at 45 °C under normal pressure for 24 h. The solid material was filtered off followed by removal of the solvent under

vacuum. The obtained solid material was recrystallized from DCM : methanol mixture (1:3) to give the pure hydroxy compound **3/n**.

3/6. Yield 84.49%, white crystals, m.p.~ 125-127 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 4H, Ar-H), 7.70 – 7.55 (m, 5H, Ar-H), 7.42 (s, 2H, Ar-H), 7.35 – 7.24 (m, 4H, Ar-H), 6.98 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.82 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar-H), 6.25 (s, 1H, Ar-OH), 4.13 – 3.98 (m, 6H, -OCH₂CH₂), 1.88 – 1.69 (m, 6H, -OCH₂CH₂CH₂), 1.64 – 1.27 (m, 18H, CH₂), 0.99 – 0.80 (m, 9H, CH₃).

3/10. Yield 84.99%, white crystals, m.p.~ 44-46 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 4H, Ar-H), 7.74 – 7.55 (m, 5H, Ar-H), 7.43 (s, 2H, Ar-H), 7.38 – 7.26 (m, 4H, Ar-H), 7.00 (d, *J* = 2.3 Hz, 1H, Ar-H), 6.84 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar-H), 5.00 (s, 1H, -OH, Ar-OH), 4.15 – 4.00 (m, 6H, -OCH₂CH₂), 2.00 – 1.70 (m, 6H, -OCH₂CH₂CH₂), 1.55 – 1.10 (m, 42H, CH₂), 0.99 – 0.77 (m, 9H, CH₃).

Final HS polycatenars B6/n and B10/n. The azobenzene-based benzoic acid derivative **4/n** [S3] (1.0 mmol) was converted to its corresponding acid chloride using thionylchloride as described for **2/n**. The obtained acid chloride was dissolved in DCM followed by addition of 1.0 mmol of the hydroxy compound **3/n**, triethylamine (1.2 mmol) and a catalytic amount of pyridine. The reaction mixture was refluxed for 6 hours under an argon atmosphere and the reaction progress was checked with TLC. The crude product was isolated as described for **2/n** and purified by column chromatography using DCM followed by recrystallization from chloroform/ethanol mixture (1/1) to give the target HS molecules. The analytical data are given below.

B6/6. Yield 64.42 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.47 – 8.37 (m, 4H, Ar-H), 8.33 (d, 2H, Ar-H), 8.05 – 7.95 (m, 4H, Ar-H), 7.84 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.73 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, 2H, Ar-H), 4.14 – 3.98 (m, 8H, -OCH₂CH₂), 1.94 – 1.70 (m, 8H, -OCH₂CH₂CH₂), 1.60 – 1.27 (m, 24H, CH₂), 1.00 – 0.84 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.10, 163.53, 162.79, 162.66, 156.25, 154.88, 153.19, 152.98, 150.64, 150.17, 146.85, 143.12, 138.57, 137.99, 134.59, 134.05, 132.39, 131.41, 130.69, 130.54, 129.07, 128.30, 128.21, 125.39, 123.82, 122.69, 122.15, 121.89, 120.28, 117.33, 114.87, 114.65, 108.64, 104.24, 73.59, 69.30, 68.49, 31.72, 31.54, 30.29, 29.26, 29.11, 25.74, 25.69, 25.67, 22.66, 22.60, 22.58, 14.07, 14.01. C₇₁H₇₇O₁₂N₃ (1164.38); EA: Calc.: C, 73.24%;

H, 6.67%; N, 3.61%. Found: C, 74.19%; H, 6.60%; N, 3.57%. HRMS (m/z): [M]+Li calc. for C₇₁H₇₇O₁₂N₃Li, 1170.570; found 1170.566.

B6/8. Yield 64.50 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 1.8 Hz, 4H, Ar-H), 8.33 (d, *J* = 6.3 Hz, 2H, Ar-H), 8.10 – 7.90 (m, 4H, Ar-H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, *J* = 7.4 Hz, 2H, Ar-H), 4.16 – 3.98 (m, 8H, -OCH₂CH₂), 1.95 – 1.69 (m, 8H, -OCH₂CH₂CH₂), 1.67 – 1.16 (m, 30H, CH₂), 1.00 – 0.80 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 164.10, 163.53, 153.21, 152.98, 138.01, 134.06, 132.41, 131.43, 130.69, 130.54, 128.30, 128.26, 128.21, 122.15, 121.88, 117.33, 108.63, 104.24, 73.59, 69.30, 68.52, 31.79, 31.72, 31.64, 31.55, 30.29, 29.32, 29.26, 29.21, 29.15, 26.00, 25.74, 25.69, 25.65, 22.67, 22.64, 22.61, 22.60, 22.58, 14.08, 14.07, 14.04, 14.01. C₇₃H₈₁O₁₂N₃ (1192.44); EA: Calc.: C, 73.53%; H, 6.85%; N, 3.52%. Found: C, 73.48%; H, 6.79%; N, 3.48%. HRMS (m/z): [M]+Li calc. for C₇₃H₈₁O₁₂N₃Li, 1198.60; found 1198.597.

B6/10. Yield 63.99 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.37 (m, 4H, Ar-H), 8.33 (d, *J* = 8.0 Hz, 2H, Ar-H), 8.06 – 7.93 (m, 4H, Ar-H), 7.84 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.15 – 3.97 (m, 8H, -OCH₂CH₂), 1.92 – 1.70 (m, 8H, -OCH₂CH₂CH₂), 1.63 – 1.17 (m, 34H, CH₂), 0.99 – 0.77 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 162.79, 154.88, 153.20, 152.98, 132.41, 131.42, 130.69, 130.54, 128.31, 128.21, 122.15, 122.05, 121.88, 108.64, 104.25, 73.59, 69.30, 68.52, 31.88, 31.72, 31.54, 30.29, 30.14, 29.55, 29.54, 29.36, 29.30, 29.26, 29.15, 25.99, 25.74, 25.69, 22.65, 22.60, 14.09, 14.07, 14.04, 14.00. C₇₅H₈₅O₁₂N₃ (1220.49); EA: Calc.: C, 73.81%; H, 7.02%; N, 3.44%. Found: C, 73.79%; H, 6.97%; N, 3.42%. HRMS (m/z): [M]+Li calc. for C₇₅H₈₅O₁₂N₃Li, 1226.630; found 1226.628.

B6/12. Yield 63.79 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.37 (m, 4H, Ar-H), 8.33 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.05 – 7.94 (m, 4H, Ar-H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.73 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.41 – 7.28 (m, 5H, Ar-H), 7.04 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.15 – 4.00 (m, 8H, -OCH₂CH₂), 1.95 – 1.69 (m, 8H, -OCH₂CH₂CH₂), 1.64 – 1.20 (m, 38H, CH₂), 1.00 – 0.82 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 166.12, 165.04, 164.10, 163.53, 162.79, 162.67, 156.24, 154.88, 153.19, 152.98, 150.63, 150.17, 146.84, 143.10, 138.57, 138.01, 137.99, 134.59, 134.06, 132.39, 131.42, 130.69, 130.54, 130.43, 129.07, 128.34, 128.32, 128.25, 128.22, 125.41, 123.82, 122.69, 122.15, 122.05, 121.88, 120.28, 117.33, 114.88, 108.64, 104.24, 81.43,

73.59, 69.30, 68.50, 31.88, 31.71, 30.29, 30.14, 29.55, 29.54, 29.36, 29.30, 29.26, 29.14, 25.99, 25.74, 25.73, 25.69, 25.63, 22.66, 22.63, 22.61, 14.09, 14.07, 14.04, 14.01, 13.99. $C_{77}H_{89}O_{12}N_3$ (1248.54); EA: Calc.: C, 74.07%; H, 7.18%; N, 3.37%. Found: C, 74.05%; H, 7.14%; N, 3.33%. HRMS (m/z): [M]+Li calc. for $C_{77}H_{89}O_{12}N_3Li$, 1254.66; found 1254.66.

B6/14. Yield 63.85 %, orange crystals. 1H NMR (500 MHz, Chloroform-*d*) δ 8.48 – 8.37 (m, 4H, Ar-H), 8.34 (d, $J = 8.1, 4.5$ Hz, 2H, Ar-H), 8.04 – 7.92 (m, 4H, Ar-H), 7.84 (d, $J = 8.6$ Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.41 – 7.28 (m, 5H, Ar-H), 7.04 (d, $J = 8.0$ Hz, 2H, Ar-H), 4.15 – 3.97 (m, 8H, $-OCH_2CH_2$), 1.96 – 1.69 (m, 8H, $-OCH_2CH_2CH_2$), 1.62 – 1.15 (m, 42H, CH_2), 1.01 – 0.65 (m, 12H, $-CH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 16504, 164.11, 163.52, 154.88, 153.20, 152.98, 150.64, 150.17, 146.83, 143.11, 138.57, 137.99, 134.59, 134.05, 132.39, 132.42, 131.42, 130.69, 130.54, 129.08, 128.31, 128.21, 123.82, 122.71, 122.15, 122.05, 121.88, 120.28, 117.33, 114.89, 108.64, 104.24, 74.27, 74.11, 73.59, 69.30, 68.52, 31.91, 31.72, 31.63, 31.54, 30.29, 30.14, 29.64, 29.58, 29.55, 29.36, 29.35, 29.26, 29.15, 25.99, 25.74, 25.70, 25.64, 22.68, 22.60, 14.10, 14.07, 14.00, 13.99. $C_{79}H_{93}O_{12}N_3$ (1276.60); EA: Calc.: C, 74.33%; H, 7.34%; N, 3.29%. Found: C, 74.27%; H, 7.32%; N, 3.28%. HRMS (m/z): [M]+Li calcd. for $C_{79}H_{93}O_{12}N_3Li$, 1282.69; found 1282.69. HRMS (m/z): [M]+Li calc. for $C_{79}H_{63}O_{12}N_3Li$, 1252.460; found 1252.458.

B6/16. Yield 63.99 %, orange crystals. 1H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.38 (m, 4H, Ar-H), 8.36 – 8.30 (m, 2H, Ar-H), 8.04 – 7.94 (m, 4H, Ar-H), 7.84 (d, $J = 8.6$ Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.27 (m, 5H, Ar-H), 7.04 (d, 2H, Ar-H), 4.13 – 4.01 (m, 8H, $-OCH_2CH_2$), 1.97 – 1.70 (m, 8H, $-OCH_2CH_2CH_2$), 1.62 – 1.18 (m, 46H, CH_2), 1.00 – 0.80 (m, 12H, $-CH_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.10, 162.79, 162.66, 156.25, 154.89, 153.19, 152.97, 152.25, 150.17, 146.85, 138.57, 137.99, 134.59, 131.41, 130.69, 130.54, 129.07, 128.30, 128.21, 125.39, 123.82, 122.69, 122.14, 121.89, 117.33, 114.87, 108.64, 104.24, 73.58, 69.30, 68.50, 31.92, 31.72, 31.54, 30.29, 29.68, 29.68, 29.66, 29.64, 29.58, 29.55, 29.35, 29.26, 29.14, 25.99, 25.74, 25.69, 22.68, 22.66, 14.09, 14.07, 14.00. $C_{81}H_{97}O_{12}N_3$ (1304.65); EA: Calc.: C, 74.57%; H, 7.49%; N, 3.22%. Found: C, 74.55%; H, 7.42%; N, 3.19%. HRMS (m/z): [M]+Li calc. for $C_{81}H_{97}O_{12}N_3Li$, 1310.720; found 1310.719.

B10/6. Yield 65.55 %, orange crystals. 1H NMR (500 MHz, Chloroform-*d*) δ 8.45 – 8.37 (m, 4H, Ar-H), 8.33 (d, $J = 8.3$ Hz, 2H, Ar-H), 8.06 – 7.93 (m, 4H, Ar-H), 7.84 (d, $J = 8.5$ Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.41 –

7.28 (m, 5H, Ar-H), 7.04 (d, 2H, Ar-H), 4.21 – 3.96 (m, 8H, -OCH₂CH₂), 1.94 – 1.71 (m, 8H, -OCH₂CH₂CH₂), 1.65 – 1.12 (m, 48H, CH₂), 1.03 – 0.79 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.10, 163.53, 162.69, 156.22, 152.97, 150.63, 150.17, 146.84, 143.11, 138.57, 137.99, 134.59, 134.06, 132.39, 131.41, 130.69, 130.54, 129.08, 128.30, 128.20, 125.43, 122.81, 122.69, 122.15, 121.89, 120.28, 117.33, 114.88, 114.64, 108.65, 104.24, 73.59, 69.30, 68.50, 31.93, 31.89, 31.54, 30.35, 29.72, 29.66, 29.632, 29.57, 29.56, 29.39, 29.33, 29.31, 29.11, 26.09, 26.05, 25.67, 22.69, 22.67, 22.58, 14.09, 14.01. C₈₃H₁₀₁O₁₂N₃ (1332.70); EA: Calc.: C, 74.80%; H, 7.64%; N, 3.15%. Found: C, 74.69%; H, 7.60%; N, 3.11%. HRMS (m/z): [M]⁺Li calc. for C₈₃H₁₀₁O₁₂N₃Li, 1338.750; found 1338.750.

B10/8. Yield 64.98 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.45 – 8.38 (m, 4H, Ar-H), 8.33 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.05 – 7.92 (m, 4H, Ar-H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.27 (m, 5H, Ar-H), 7.04 (d, *J* = 8.5 Hz, 2H, Ar-H), 4.16 – 3.99 (m, 8H, -OCH₂CH₂), 1.96 – 1.69 (m, 8H, -OCH₂CH₂CH₂), 1.66 – 1.14 (m, 52H, CH₂), 0.98 – 0.79 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.10, 163.53, 162.79, 162.68, 154.88, 153.19, 152.98, 150.17, 146.84, 138.57, 137.99, 134.59, 134.06, 132.39, 131.42, 130.69, 130.54, 129.07, 128.30, 128.21, 125.42, 123.81, 122.69, 122.15, 121.89, 120.28, 117.33, 114.88, 114.65, 108.65, 104.24, 73.59, 69.30, 68.51, 31.93, 31.89, 31.79, 30.35, 29.72, 29.66, 29.62, 29.57, 29.56, 29.38, 29.34, 29.33, 29.31, 29.21, 29.15, 26.08, 26.05, 26.00, 22.69, 22.67, 22.64, 14.09, 14.08. C₈₅H₁₀₅O₁₂N₃ (1360.76); EA: Calc.: C, 75.03%; H, 7.78%; N, 3.09%. Found: C, 74.97%; H, 7.77%; N, 3.0%. HRMS (m/z): [M]⁺Li calc. for C₈₅H₁₀₅O₁₂N₃Li, 1366.790; found 1366.788.

B10/10. Yield 64.84 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.38 (m, 4H, Ar-H), 8.33 (d, *J* = 7.5 Hz, 2H, Ar-H), 8.06 – 7.92 (m, 4H, Ar-H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.72 – 7.63 (m, 4H, Ar-H), 7.61 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.20 – 3.83 (m, 8H, -OCH₂CH₂), 1.96 – 1.70 (m, 8H, -OCH₂CH₂CH₂), 1.69 – 1.11 (m, 56H, CH₂), 0.97 – 0.77 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 164.10, 163.53, 162.79, 152.97, 146.83, 131.42, 130.69, 130.54, 128.30, 128.21, 122.15, 121.89, 117.33, 108.65, 73.59, 69.31, 31.90, 31.88, 30.34, 29.72, 29.66, 29.57, 29.56, 9.54, 29.38, 29.36, 29.33, 29.30, 29.14, 26.08, 26.05, 25.99, 22.69, 22.67, 14.09. C₈₇H₁₀₉O₁₂N₃ (1388.81); EA: Calc.: C, 75.24%; H, 7.91%; N, 3.03%. Found: C, 75.17%; H, 7.86%; N, 2.98%. HRMS (m/z): [M]⁺Li calc. for C₈₇H₁₀₉O₁₂N₃Li, 1394.82; found 1394.81.

B10/12. Yield 65.00 %, orange crystals. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.37 (m, 4H, Ar-H), 8.33 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.04 – 7.94 (m, 4H, Ar-H), 7.84 (d, $J = 8.6$ Hz, 1H, Ar-H), 7.71 – 7.62 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, $J = 8.6$ Hz, 2H, Ar-H), 4.15 – 4.00 (m, 8H, $-\text{OCH}_2\text{CH}_2$), 1.96 – 1.70 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.68 – 1.16 (m, 60H, CH_2), 0.97 – 0.81 (m, 12H, $-\text{CH}_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.10, 163.53, 162.78, 156.22, 154.88, 153.19, 152.97, 150.63, 150.17, 146.83, 138.57, 137.99, 134.59, 134.06, 132.39, 131.42, 130.69, 130.54, 129.07, 128.30, 128.21, 125.42, 123.81, 122.69, 122.15, 121.89, 117.33, 114.88, 108.64, 104.24, 73.59, 69.30, 68.51, 31.93, 31.89, 31.88, 30.35, 29.72, 29.66, 29.62, 29.57, 29.56, 29.55, 29.54, 29.39, 29.36, 29.33, 29.30, 29.14, 26.08, 26.05, 25.99, 22.69, 22.67, 14.09. $\text{C}_{89}\text{H}_{113}\text{O}_{12}\text{N}_3$ (1416.86); EA: Calc.: C, 75.45%; H, 8.04%; N, 2.97%. Found: C, 75.40%; H, 7.99%; N, 2.96%. HRMS (m/z): $[\text{M}] + \text{Li}$ calc. for $\text{C}_{89}\text{H}_{113}\text{O}_{12}\text{N}_3\text{Li}$, 1422.850; found 1422.847.

B10/14. Yield 65.02 %, orange crystals. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.37 (m, 4H, Ar-H), 8.33 (d, 2H, Ar-H), 8.05 – 7.93 (m, 4H, Ar-H), 7.84 (d, $J = 8.6$ Hz, 1H, Ar-H), 7.73 – 7.63 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, $J = 8.3$ Hz, 2H, Ar-H), 4.12 – 3.99 (m, 8H, $-\text{OCH}_2\text{CH}_2$), 1.98 – 1.70 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.68 – 1.13 (m, 64H, CH_2), 0.96 – 0.80 (m, 12H, $-\text{CH}_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.11, 163.53, 162.79, 154.88, 153.19, 152.97, 150.17, 146.84, 143.11, 138.57, 137.99, 134.59, 134.05, 132.39, 131.42, 130.69, 130.54, 128.30, 128.21, 125.41, 123.81, 122.71, 122.15, 121.90, 117.33, 114.88, 108.65, 104.24, 73.59, 69.30, 68.51, 31.93, 31.89, 30.35, 29.72, 29.68, 29.66, 29.64, 29.62, 29.57, 29.56, 29.55, 29.38, 29.36, 29.34, 29.31, 29.14, 26.08, 26.05, 25.99, 22.69, 22.67, 14.09, 14.08. $\text{C}_{91}\text{H}_{117}\text{O}_{12}\text{N}_3$ (1444.92); EA: Calc.: C, 75.64%; H, 8.16%; N, 2.85%. Found: C, 75.58%; H, 8.11%; N, 2.82%. HRMS (m/z): $[\text{M}] + \text{Li}$ calc. for $\text{C}_{91}\text{H}_{117}\text{O}_{12}\text{N}_3\text{Li}$, 1450.88; found 1450.87.

B10/16. Yield 66.21 %, orange crystals. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.46 – 8.38 (m, 4H, Ar-H), 8.33 (d, 2H, Ar-H), 8.04 – 7.94 (m, 4H, Ar-H), 7.84 (d, $J = 8.5$ Hz, 1H, Ar-H), 7.71 – 7.63 (m, 4H, Ar-H), 7.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.44 (s, 2H, Ar-H), 7.42 – 7.28 (m, 5H, Ar-H), 7.04 (d, 2H, Ar-H), 4.13 – 3.99 (m, 8H, $-\text{OCH}_2\text{CH}_2$), 1.93 – 1.71 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.65 – 1.17 (m, 68H, CH_2), 0.96 – 0.80 (m, 12H, $-\text{CH}_3$). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.04, 164.11, 163.53, 162.68, 156.25, 154.88, 153.19, 152.97, 150.63, 150.17, 146.85, 143.11, 137.99, 134.59, 134.06, 132.39, 131.41, 130.69, 130.54, 129.07, 128.30, 128.21, 125.39, 123.81, 122.69, 122.15, 121.89, 117.33, 114.87, 108.65, 104.24, 73.59, 69.30, 68.50, 31.93, 31.92, 31.89, 30.34, 29.72, 29.68, 29.66, 29.64, 29.62, 29.57, 29.56, 29.38,

29.36, 29.34, 29.31, 29.14, 26.08, 26.05, 25.99, 22.69, 22.67, 14.09. C₉₃H₁₂₁O₁₂N₃ (1472.97); EA: Calc.: C, 75.83%; H, 8.28%; N, 2.85%. Found: C, 75.81%; H, 8.26%; N, 2.79%. HRMS (m/z): [M]⁺Li calc. for C₉₃H₁₂₁O₁₂N₃Li, 1478.91; found 1478.91.

B10/22. Yield 66.39 %, orange crystals. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.45 – 8.37 (m, 4H, Ar-H), 8.32 (d, 2H, Ar-H), 8.02 – 7.94 (m, 4H, Ar-H), 7.84 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.72 – 7.62 (m, 4H, Ar-H), 7.60 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.43 (s, 2H, Ar-H), 7.40 – 7.27 (m, 5H, Ar-H), 7.03 (d, 2H, Ar-H), 4.13 – 3.99 (m, 8H, -OCH₂CH₂), 1.97 – 1.68 (m, 8H, -OCH₂CH₂CH₂), 1.64 – 1.14 (m, 80H, CH₂), 0.97 – 0.77 (m, 12H, -CH₃). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.05, 164.11, 163.54, 162.79, 162.68, 156.24, 154.89, 153.21, 152.99, 150.65, 150.18, 146.85, 143.13, 138.58, 137.99, 134.60, 134.06, 132.40, 131.42, 130.69, 130.55, 129.08, 128.31, 128.25, 128.21, 125.41, 123.82, 122.70, 122.16, 122.05, 121.89, 120.28, 117.34, 114.88, 114.65, 108.66, 104.24, 73.59, 69.31, 68.50, 31.93, 31.89, 30.35, 30.29, 30.19, 29.77, 29.72, 29.68, 29.66, 29.64, 29.62, 29.57, 29.55, 29.54, 29.49, 29.38, 29.36, 29.33, 29.31, 29.21, 29.15, 26.9, 26.08, 26.05, 26.01, 25.99, 22.69, 22.67, 14.09. C₉₉H₁₃₃O₁₂N₃ (1557.13); EA: Calc.: C, 76.36%; H, 8.61%; N, 2.70%. Found: C, 76.33%; H, 8.60%; N, 2.66%. HRMS (m/z): [M]⁺Li calc. for C₉₉H₁₃₃O₁₂N₃Li, 1564.01; found 1564.00.

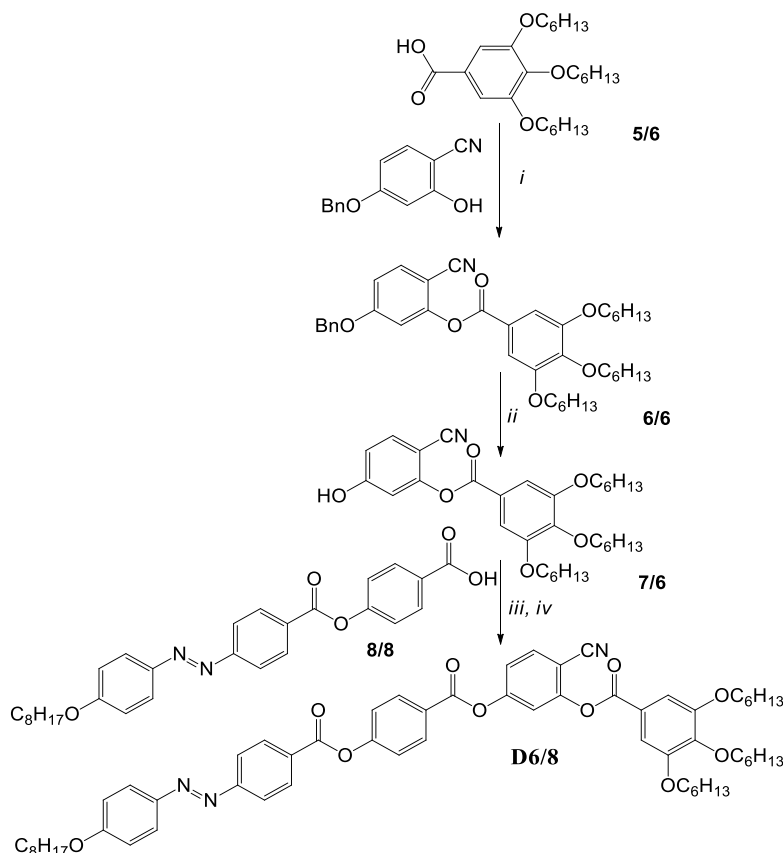
1. 3. Synthesis of compound D6/8

The synthesis of compound **D6/8** is shown in Scheme S1.

6/6. The acid **5/6** [S4] (0.58 g, 1.37 mmol), a catalytic amount of DMAP and 4-benzyloxy-2-hydroxybenzotrile (0.31 g, 1.37 mmol) were dissolved in dichloromethane under stirring and DCC (0.35 g, 1.67 mmol) previously dissolved in DCM was added and the stirring was continued for 24 hours. The white by-product was filtered out and washed several times with DCM. The solvent was removed, and the crude white material obtained was recrystallized from methanol to give 85.60 % yield of compound **6/6** as colourless crystals. M.p. ~ 79-80 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.48 – 7.28 (m, 7H, Ar-H), 7.12 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 5.12 (s, 2H, -OCH₂ph), 4.24 – 3.87 (m, 6H, -OCH₂CH₂), 1.92 – 1.69 (m, 6H, -OCH₂CH₂CH₂-), 1.63 – 1.25 (m, 18H, -CH₂-), 0.97 – 0.86 (m, 9H, -CH₃).

7/n. This was synthesized as described for **3/n**. No further purification was required. Yield 92.30%, colourless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.43 (s, 2H, Ar-H), 6.90 (d, *J* = 2.3 Hz, 1H, Ar-H), 6.79 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar-H), 6.34

(s, 1H, Ar-OH), 4.10 – 3.99 (m, 6H, $-\text{OCH}_2\text{CH}_2$), 1.87 – 1.70 (m, 6H, $-\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.54 – 1.26 (m, 18H, $-\text{CH}_2-$), 0.97 – 0.86 (m, 9H, $-\text{CH}_3$).



Scheme S1. Synthesis of compound **D6/8**. Reagents and conditions: *i*) DCC, DMAP, dry CH_2Cl_2 , stirring 24 hr.; *ii*) H_2 , Pd/C-10%, dry THF, stirring 24 hr; *iii*) DMF, SOCl_2 , reflux 1 hr.; *iv*) dry CH_2Cl_2 , dry TEA, dry pyridine, reflux for 6 hr.

D6/8. Synthesized as described for the final HS polycatenars **B6/n** and **B10/n**. The azobenzene-based benzoic acid (**8/n**)[S5] (0.08 g, 0.17 mmol) was converted to the corresponding benzoyl chloride and after removal of excess thionyl chloride (0.09g, 0.17 mmol) of **7/n** was added followed by addition of triethylamine (0.03, 1.2 mmol) and few drops of dry pyridine and stirred under reflux for 6 hrs. The work-up of the reaction was done in analogous way described for **B6/n** and **B10/n**. The final compound was purified by column chromatography using DCM followed by recrystallization from ethanol:chloroform mixture (8:2) to yield 65.49 % of **D6/8** as an orange powder. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.39 – 8.24 (m, 4H, Ar-H), 8.03 – 7.94 (m, 4H, Ar-H), 7.79 (d, $J = 8.5$ Hz, 1H, Ar-H), 7.55 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.50 – 7.40 (m, 4H, Ar-H), 7.31 (dd, $J = 8.5, 2.2$ Hz, 1H, Ar-H), 7.03 (d, $J = 8.5$ Hz, 2H, Ar-H), 4.12 – 4.00 (m, 8H, $-\text{OCH}_2\text{CH}_2$), 1.90 – 1.70 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.65 – 1.18 (m, 28H, $-\text{CH}_2$), 1.01 – 0.82 (m, 12H, CH_3). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.05, 163.39, 163.25, 162.61, 156.10, 155.65, 154.73, 153.76, 153.08, 146.86, 143.73, 133.88, 132.08, 131.36, 131.33, 129.66, 126.06, 125.36, 122.79, 122.63, 122.27, 122.24, 119.77, 117.31, 114.87, 108.89,

104.33, 73.62, 69.27, 68.50, 31.79, 31.70, 31.53, 30.27, 29.32, 29.57, 29.21, 29.15, 25.99, 25.91, 25.72, 22.65, 22.64, 22.59, 14.07, 14.05, 13.99. **C₆₀H₇₃O₁₀N₃ (996.24)**; EA: Calc.: C, 72.34%; H, 7.39%; N, 4.22%. Found: C, 72.28%; H, 7.37%; N, 4.20%. HRMS (m/z): [M]⁺Li calc. for C₆₀H₇₃O₁₀N₃Li, 1002.550; found 1002.548.

2. Representative NMR Spectra

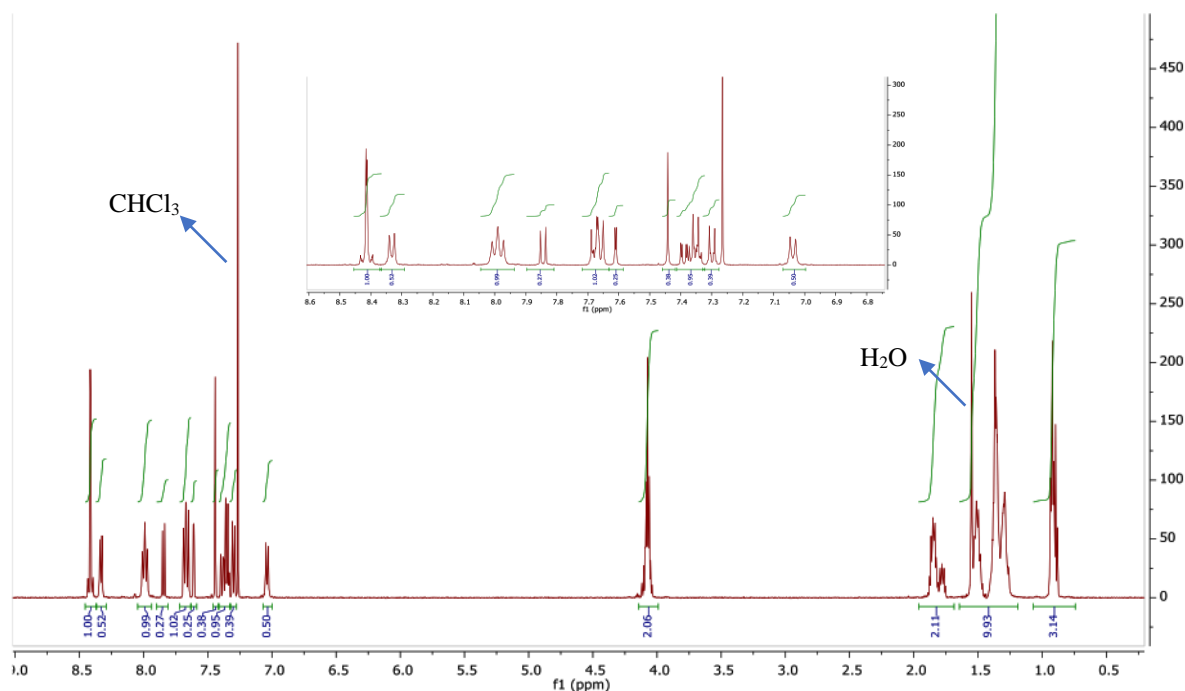


Figure S1. ¹H NMR Spectrum of **B6/12** (500 MHz, CDCl₃).

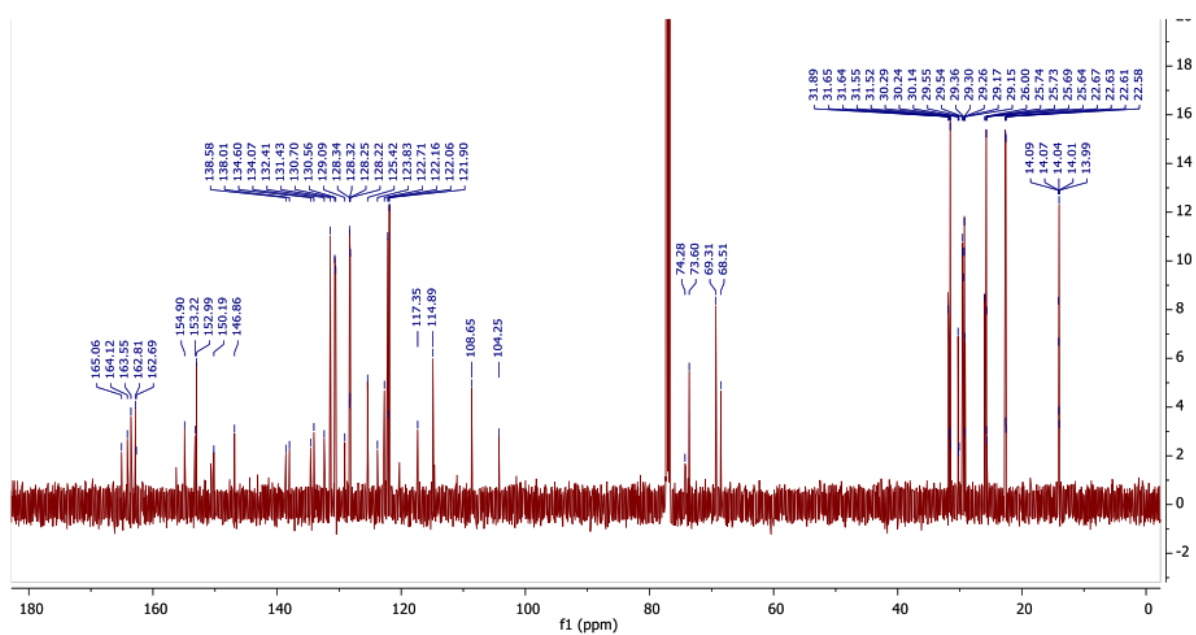


Figure S2. ¹³C NMR Spectrum of **B6/12** (126 MHz, CDCl₃).

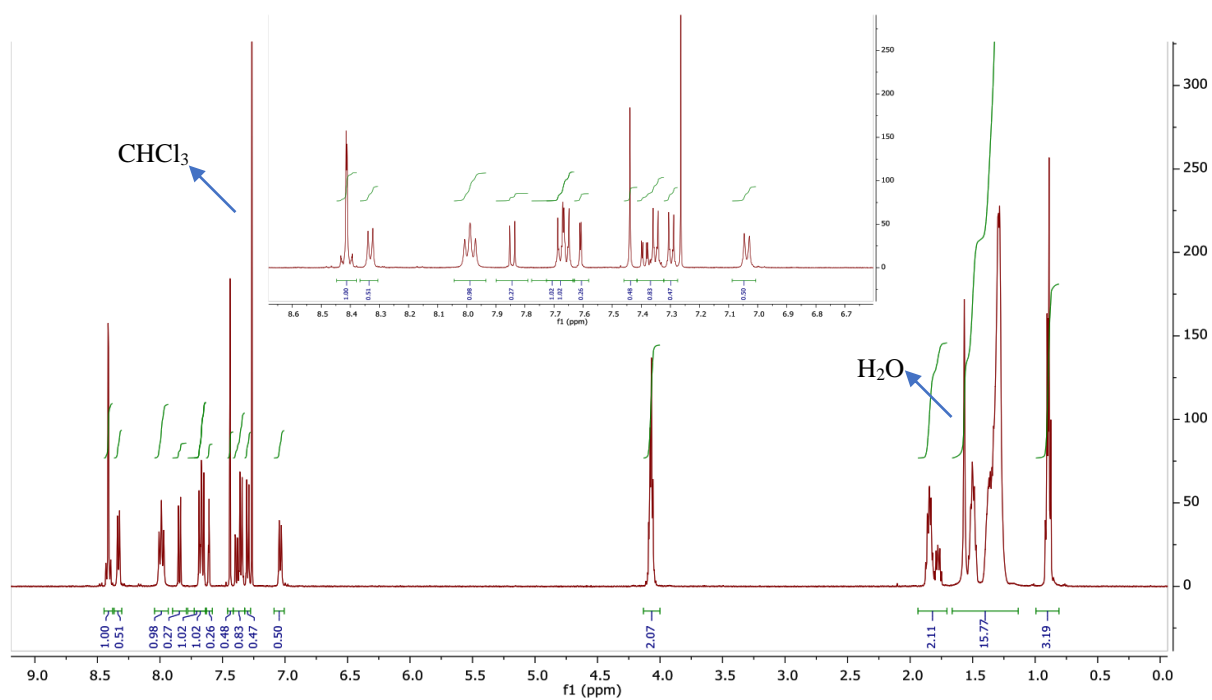


Figure S3. ¹H NMR Spectrum of B10/8 (500 MHz, CDCl₃).

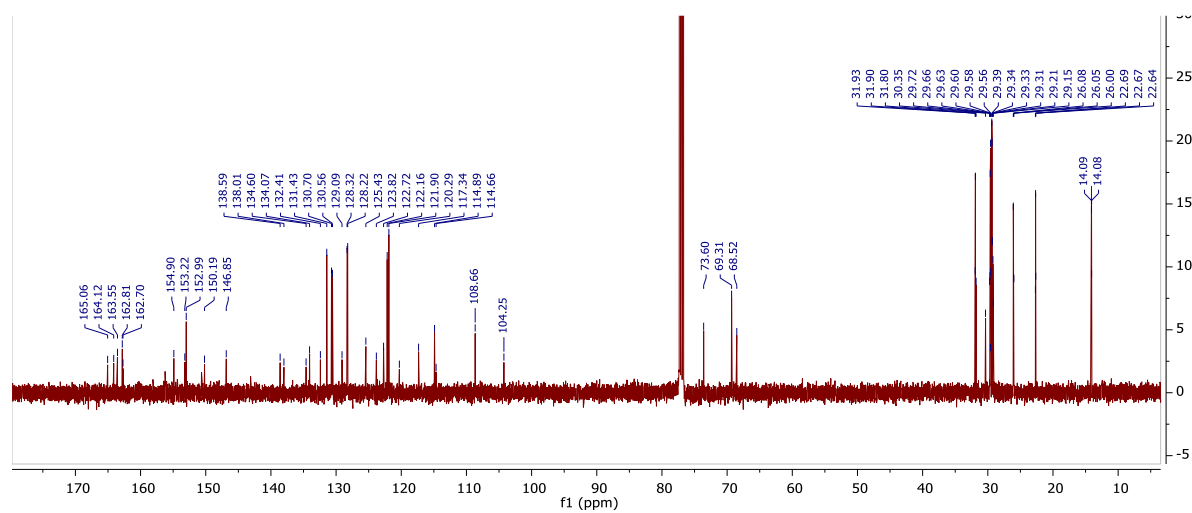


Figure S4. ¹³C NMR Spectrum of B10/8 (126 MHz, CDCl₃).

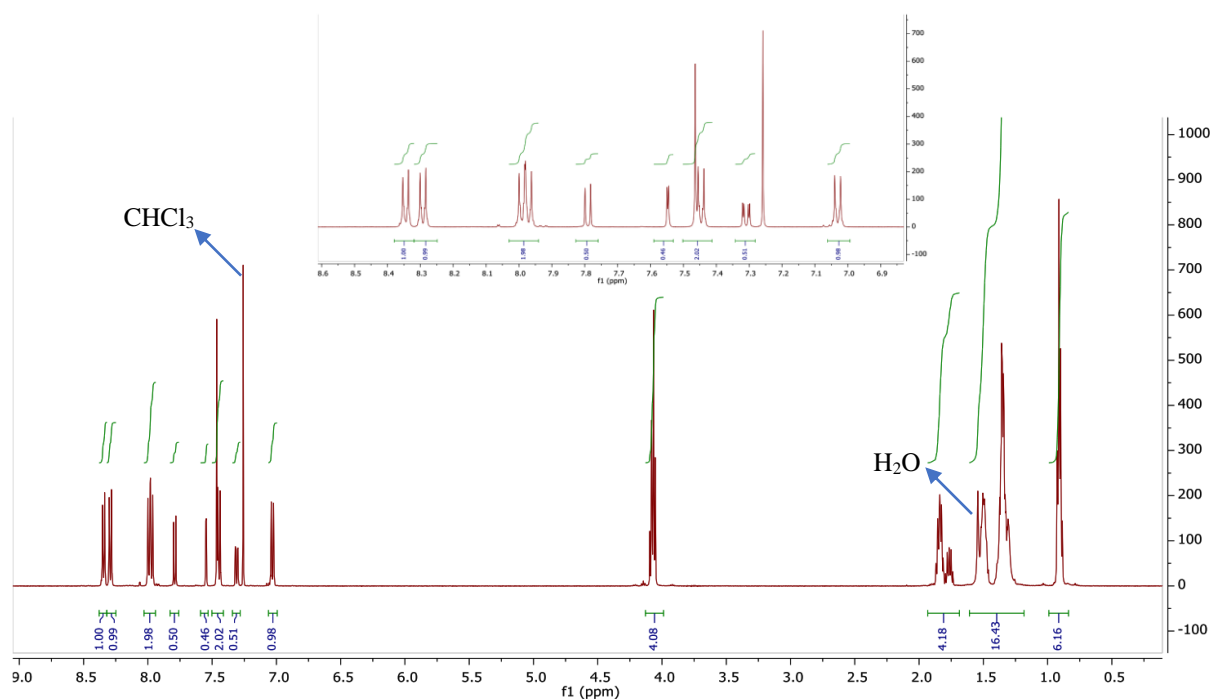


Figure S5. ¹H NMR Spectrum of D6/8 (500 MHz, CDCl₃).

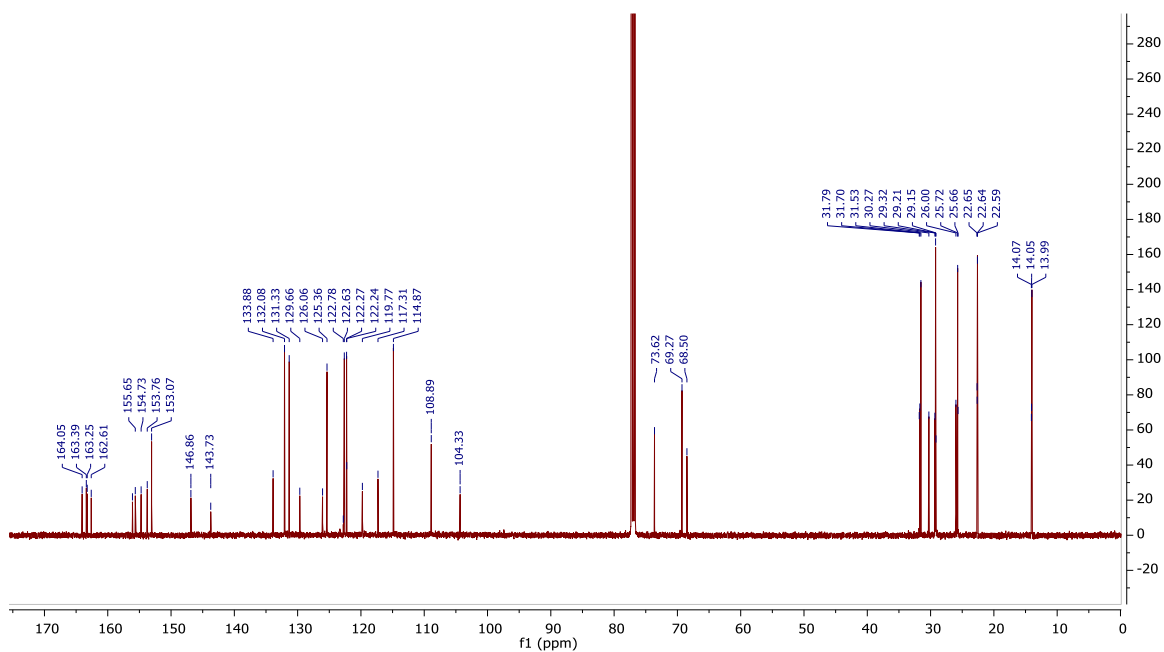


Figure S6. ¹³C NMR Spectrum of D6/8 (126 MHz, CDCl₃).

3. Experimental Method

Synchrotron small-angle X-ray scattering experiments were conducted at beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). Samples were held in evacuated 1mm diameter capillaries. Self-made hot stage and Pilatus 2M CCD are used in ALS, modified Linkam hot stage and Mar165 CCD are used in SSRF. Data calibration was conducted by silver behemate and a series of n-alkanes. The integration of 2D data to 1D plot is carried out by Irena and Nika macro on Igor64 platform with Gauss equation. Peak positions provide information to determine space group and lattice parameter. With proper indexing from space group and integrated peak intensities, we are able to reconstruct 3D electron density ($\rho(x, y, z)$) map via Fourier transform (FT) as

$$\rho(x, y, z) = \sum_{hkl} F(hkl) \exp [2\pi i(hx + ky + lz)]$$

where $F(hkl)$ is a structure factor for a peak with Miller indices (hkl) . A scattering experiment does not directly reveal the structure factor. Instead, scattering provides us with intensities I which is related with the amplitude of the structure factor:

$$I(hkl) = \kappa \cdot F(hkl) \cdot F^*(hkl) = \kappa \cdot |F(hkl)|^2$$

with κ being a coefficient related with the incident beam intensity, linear attenuation, sample volume etc. However, because the electron density map that we calculate is a relative one and the beam statue is stable during the SAXS experiment, κ is simply regarded as 1. Replacing the structure factor with intensity and phase, electron density can be calculated as:

$$\rho(x, y, z) = \sum_{hkl} \sqrt{I(hkl)} \exp [2\pi i(hx + ky + lz) + i\phi_{hkl}]$$

It is well-known that the information on the structure-factor phase ϕ_{hkl} is lost during the powder scattering. For a centrosymmetric structure, i.e. $Ia\bar{3}d$ phase, with the electron density $\rho(x, y, z) = \rho(\bar{x}, \bar{y}, \bar{z})$, the phase ϕ_{hkl} is either 0 or π . This allows us an exhaustive approach by comparing all possible phase combinations. However, for non-centrosymmetric structures, $I23$, Tet_{bi} , the phase ϕ_{hkl} is arbitrary between 0 and 2π except for a few specific Miller planes. A model-dependent simulation is needed for these structures to determine the phase ϕ_{hkl} , which will be explained later. The best combination is determined by physical merit of reconstructed electron density map and other information from system, like volume ratio of aromatic/aliphatic region. This method works well for liquid crystal system from work before, especially for systems with only few intense peaks.

4. Additional data

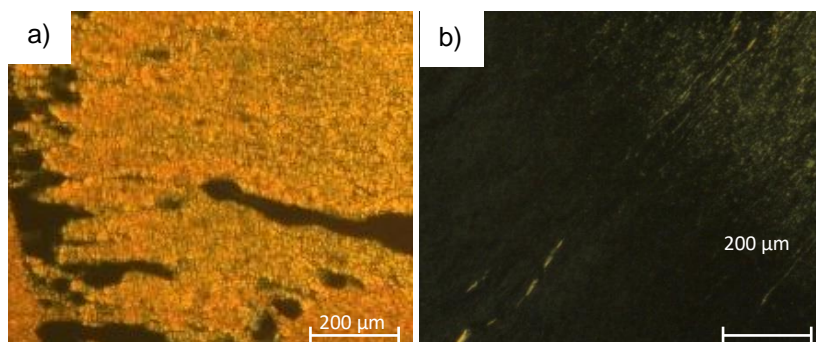


Figure S7. Optical micrographs observed in a homeotropic cell for the SmA phase of compound **B6/6** at $T = 120$ °C: a) after applying shearing stress and b) after removal shearing stress.

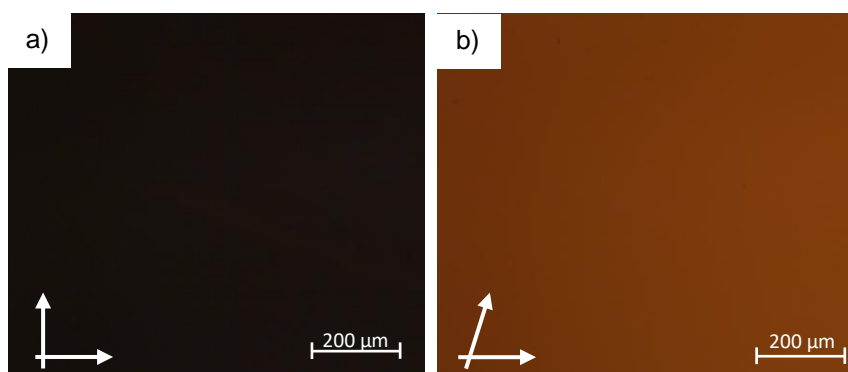


Figure S8. Optical micrographs observed in a homeotropic cell for the Cub/ $1a\bar{3}d$ phase of **B10/22** at 140 °C: a) under crossed polarizers and b) under slightly uncrossed polarizers indicating the absence of any chiral domains.

Table S1. Experimental and calculated d -spacings, relative integrated intensities, and phases used in the reconstruction of electron densities for the Cub/ $1a\bar{3}d$ phase of **B6/14** at 150 °C. All intensities values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs.}}$ - spacings (nm)	$d_{\text{cal.}}$ - spacings (nm)	<i>intensity</i>	<i>phase</i>
(211)	4.61	4.61	100.00	π
(220)	3.99	4.00	57.58	π
(321)	3.02	3.02	0.03	/
(400)	2.82	2.83	4.57	π
(420)	2.53	2.53	0.79	0
(332)	2.41	2.41	0.40	/
(422)	2.30	2.31	0.10	/
$a_{\text{cub}} = 11.30$ nm				

Table S2. Experimental and calculated d -spacings, relative integrated intensities used in the reconstruction of electron densities for the SmA phase of **B6/14** at 155 °C. All intensities values are Lorentz and multiplicity corrected.

(hk)	$d_{\text{obs.}}$ - spacings (nm)	$d_{\text{cal.}}$ - spacings (nm)	<i>intensity</i>
(10)	4.81	4.81	100.00
(20)	2.40	2.41	0.16
$d = 4.82$ nm			

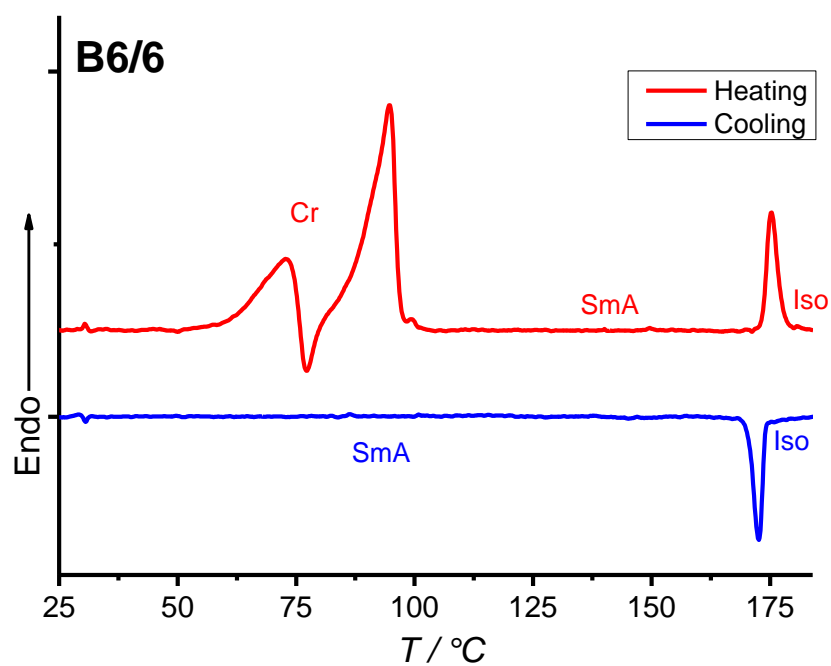


Figure S9. DSC thermograms obtained for compound **B6/6**; with 10 K min⁻¹ heating and cooling rates.

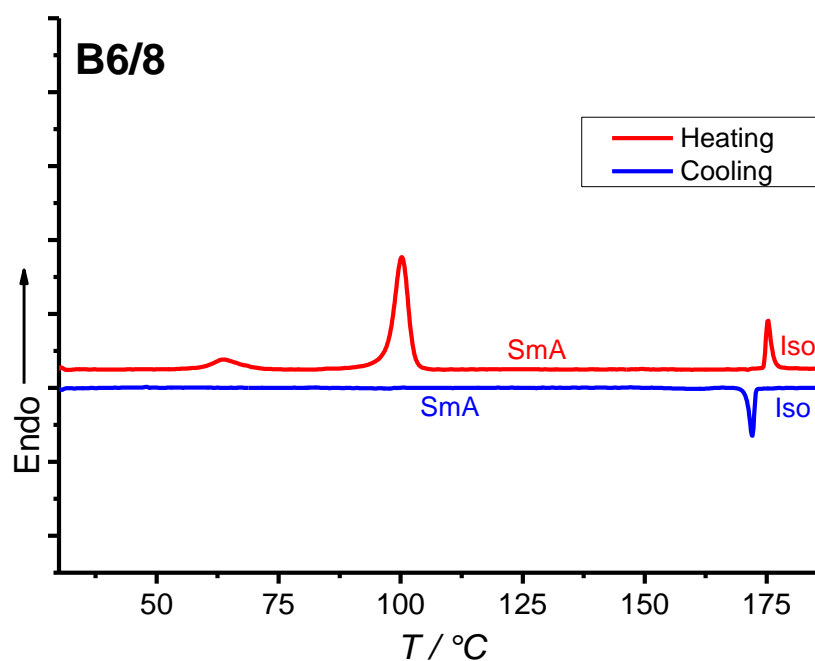


Figure S10. DSC thermograms obtained for compound **B6/8**; with 10 K min⁻¹ heating and cooling rates.

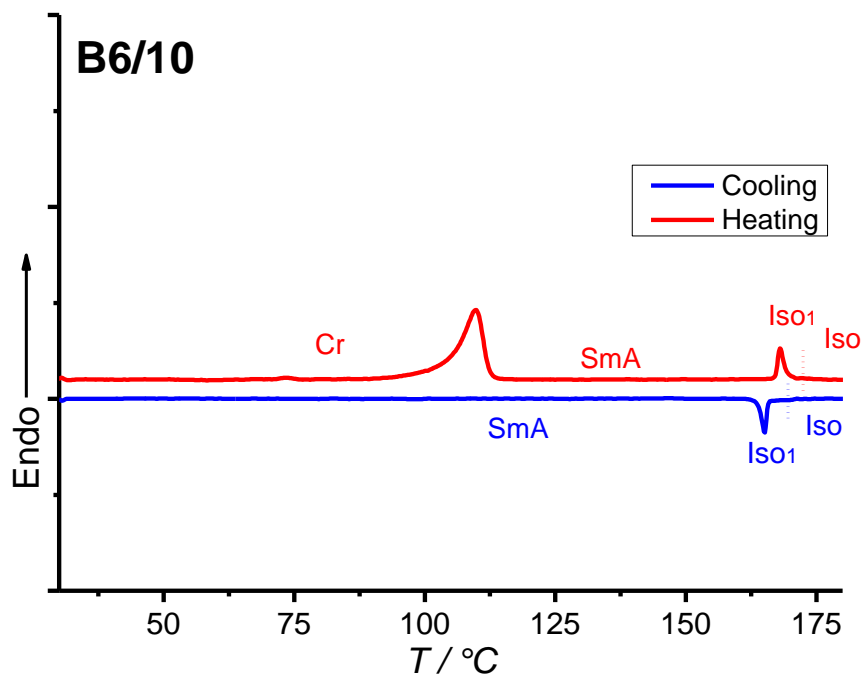


Figure S11. DSC thermograms obtained for compound **B6/10**; with 10 K min⁻¹ heating and cooling rates.

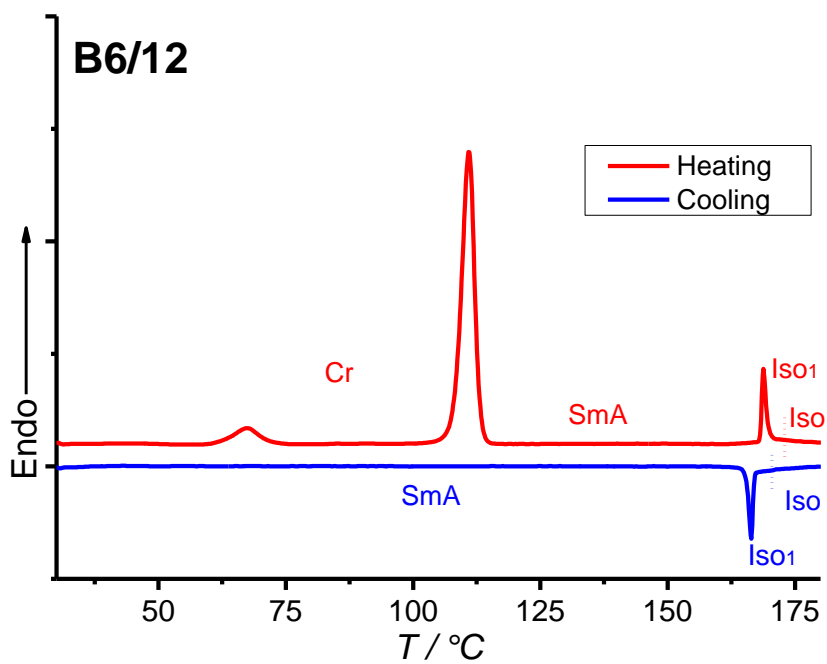


Figure S12. DSC thermograms obtained for compound **B6/12**; with 10 K min⁻¹ heating and cooling rates.

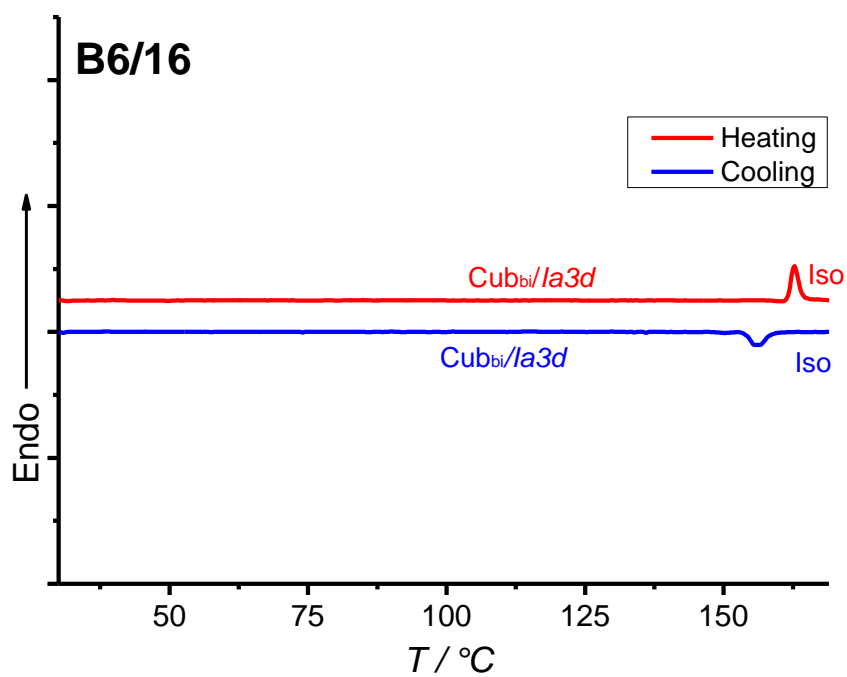


Figure S13. DSC thermograms obtained for compound **B6/16**; with 10 K min^{-1} heating and cooling rates.

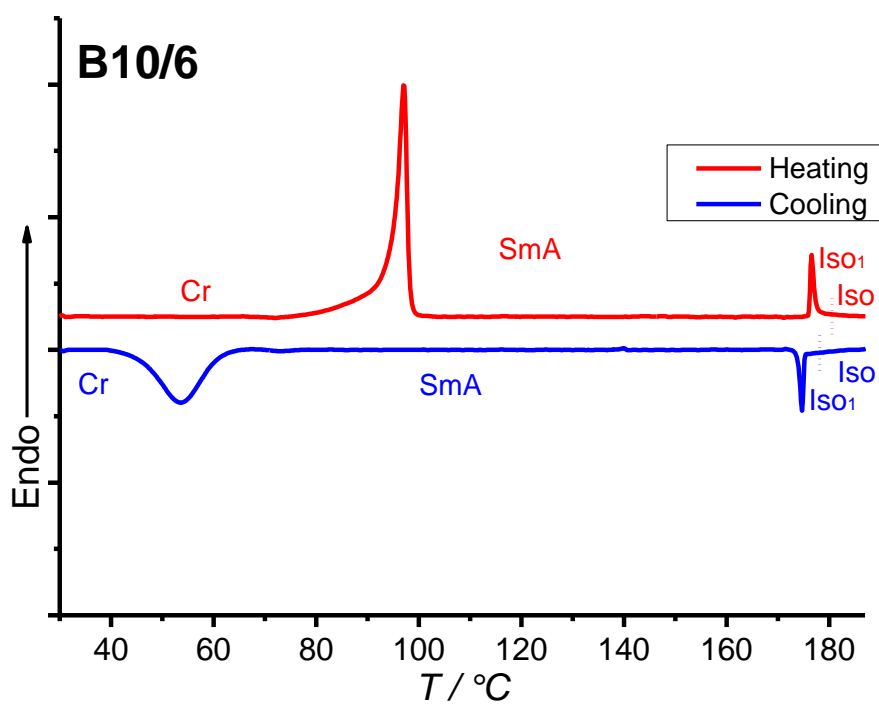


Figure S14. DSC thermograms obtained for compound **B10/6**; with 10 K min^{-1} heating and cooling rates.

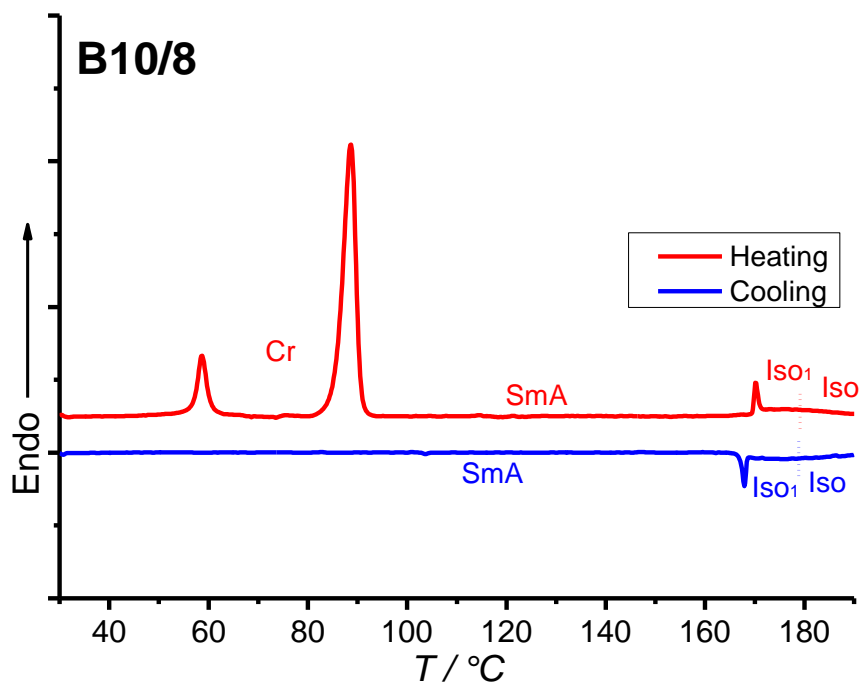


Figure S15. DSC thermograms obtained for compound **B10/8**; with 10 K min⁻¹ heating and cooling rates.

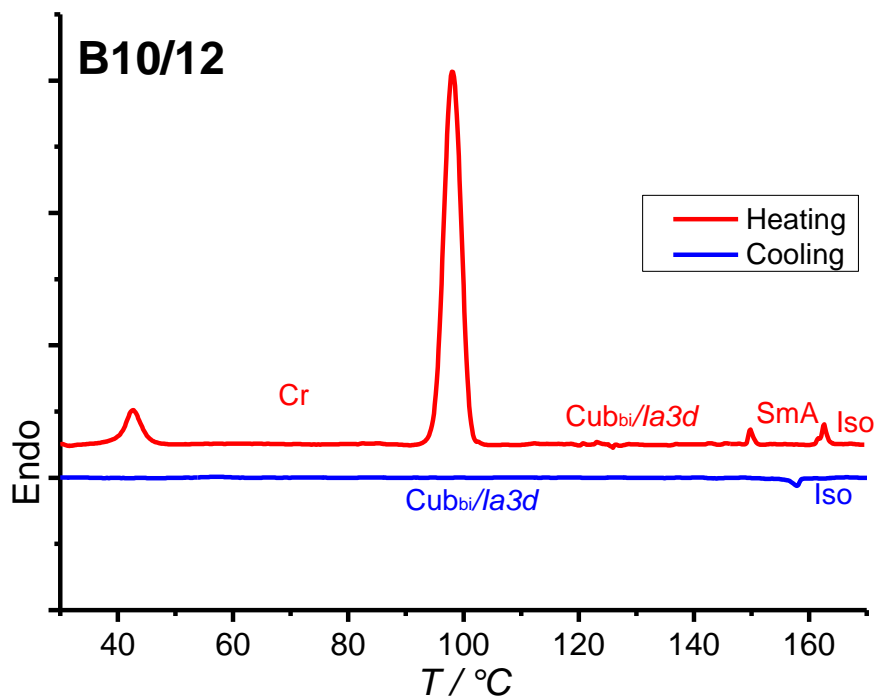


Figure S16. DSC thermograms obtained for compound **B10/12**; with 10 K min⁻¹ heating and cooling rates.

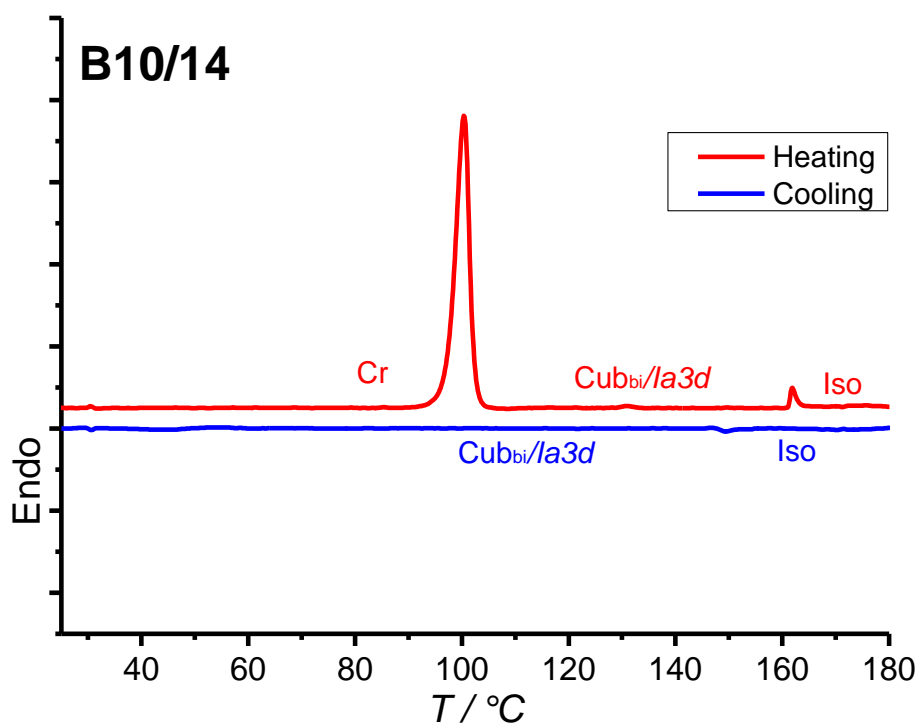


Figure S17. DSC thermograms obtained for compound **B10/14**; with 10 K min⁻¹ heating and cooling rates.

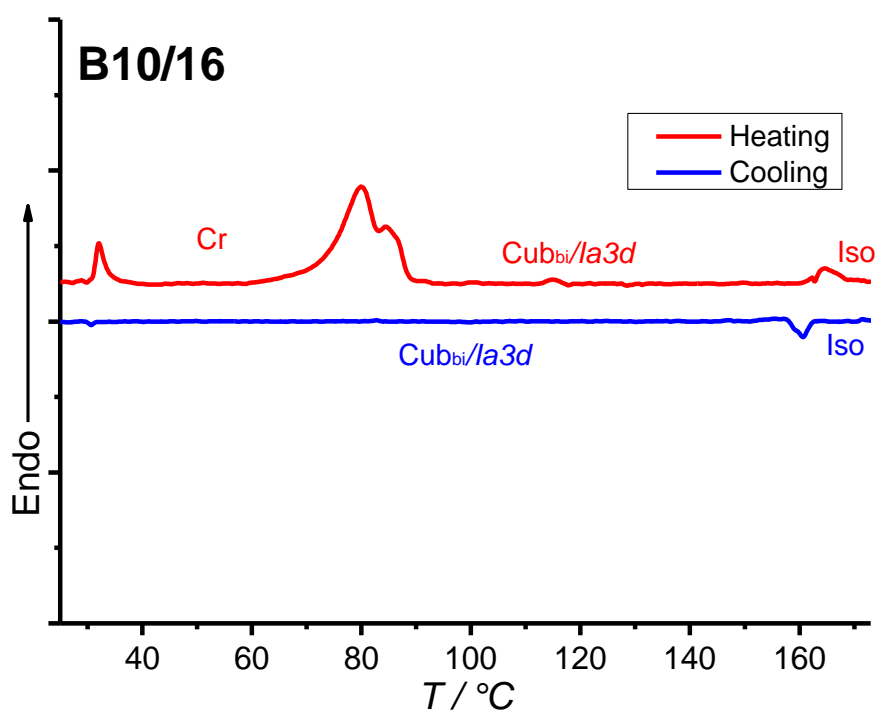


Figure S18. DSC thermograms obtained for compound **B10/16**; with 10 K min⁻¹ heating and cooling rates.

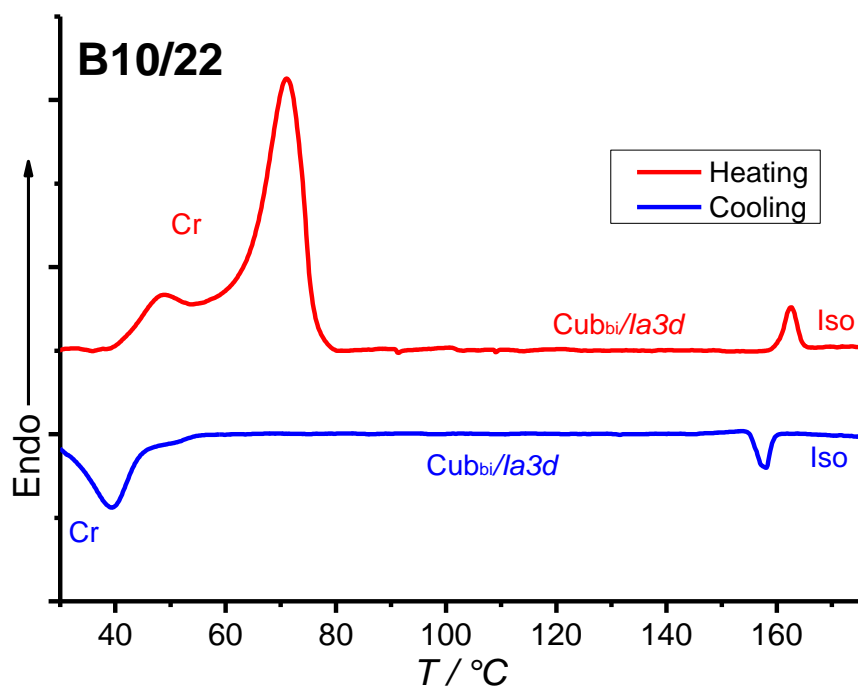


Figure S19. DSC thermograms obtained for compound **B10/22**; with 10 K min⁻¹ heating and cooling rates.

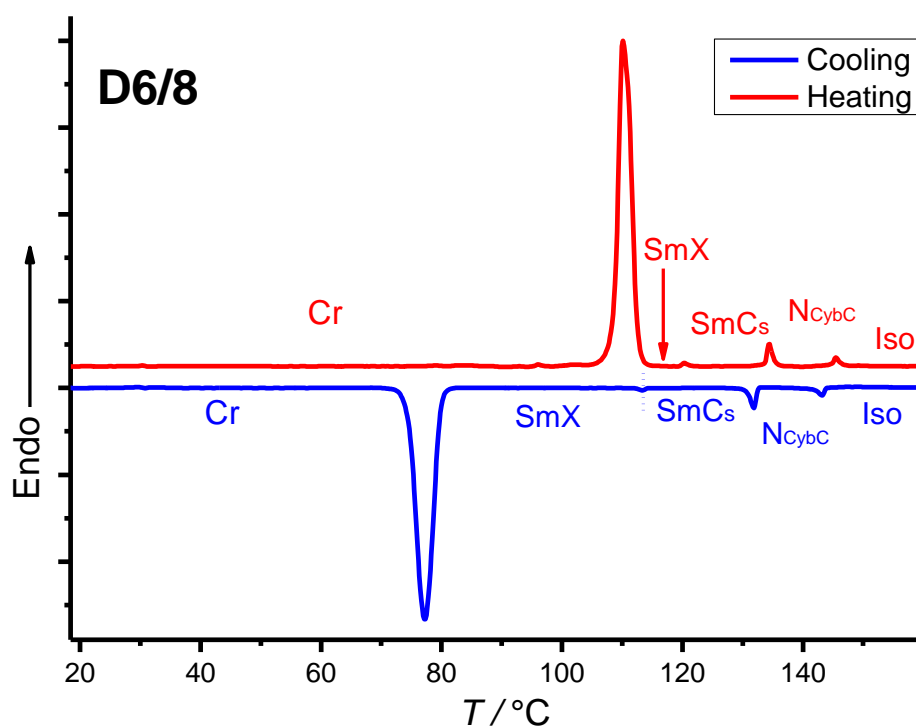


Figure S20. DSC thermograms obtained for compound **D6/8**; with 10 K min⁻¹ heating and cooling rates.

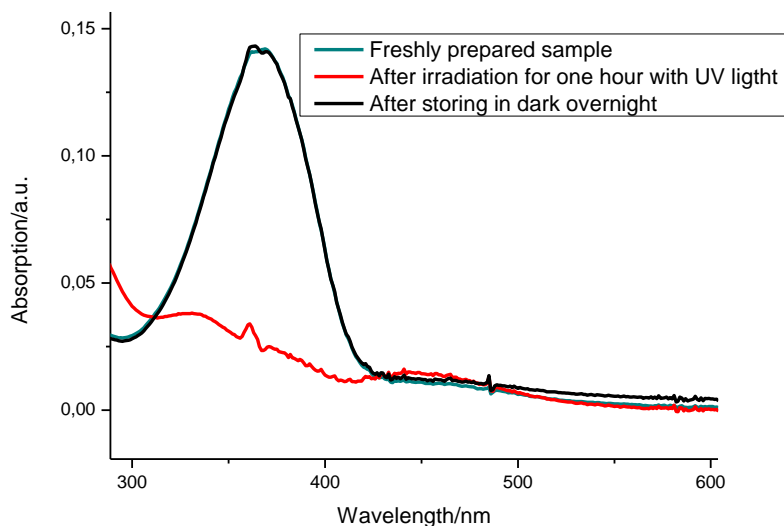


Figure S21. UV-vis spectra (absorbance vs. wavelength) of **B10/22** dissolved in chloroform.

5. References

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